

# THE NATURALLY OCCURRING CHROMATES OF LEAD

S. A. WILLIAMS

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## SYNOPSIS

The history of the natural lead chromates is traced from 1766 to 1972, and the published physical and chemical data for the several valid species are summarized. A select bibliography of the primary literature on these minerals is appended.

## INTRODUCTION

IN 1971, during work in the Mineral Department of the British Museum (Natural History) on the new mineral embreyite, I became aware that this mineral had been observed at least once before, perhaps as early as 1789, but not recognized as a distinct species. At the suggestion of Mr P. G. Embrey, I embarked on a historical study that eventually included all the known natural chromates of lead.

I have attempted to report all of the older works. Literature became voluminous in the last hundred years, and for this period I have tried to select only the more important papers. The original author's data have been quoted directly in most cases but in a few I have translated it into modern terms. Very old chemical analyses raise particular problems and if the author did not give weights obtained at every step of his procedure, but gave only final results, it was not possible to correct results using modern atomic weights. The literature is cluttered with

misquotes, misprints and other errors. I have tried to set the record straight whenever possible.

The study was made more thorough by free access to the Museum's large collection of specimens from Berezov; the material from this locality was greatly augmented by the acquisition of N. Koksharov's collection in 1865. Examination of these materials has made it easier for me to visualize what has been described in the past and to judge the nature of the material studied and the quality of work accomplished by my predecessors.

#### ACKNOWLEDGEMENTS

This study would not have been possible without access to the superb library at the British Museum (Natural History). Most references were easily found; Mr R. T. W. Atkins and Miss Julia Brown of the library of the Department of Mineralogy assisted me in finding the more obscure ones. If any early references have been missed I must accept the blame.

Miss Eva Fejer has helped me immeasurably by translating Russian in several instances. Dr Pierre Bariand generously placed the type iranite specimen, and most of his collections from Iran, at my disposal. Dr Max Hey read the manuscript with great care and also checked many of the Russian locality names. The quality of this paper has been greatly enhanced by his efforts. My thanks are especially due to Mr P. G. Embrey, not only for suggesting the study, but for helpful discussion.

#### THE HISTORICAL BACKGROUND TO THE DISCOVERY OF CHROMIUM

Lead chromate minerals were first discovered in the Berezov mines in the central Urals. Early travellers in Russia provide our first scraps of information. Marco Polo, when passing through Russia, south of the Ural Mountains, was told that there was much silver in Russia and that there were silver mines to the north. This was in about 1250 (Yule, 1921). Almost a century later Ibn Batuta also reported silver mines to the north when he travelled in the same regions as Marco Polo (Humboldt, 1843). These reports are puzzling, because although a good deal of gold was later discovered in the Urals, gold carrying six to eight per cent silver, I have seen no mention in later writings of ancient silver mines in the Urals.

The central and north Ural Mountains were sparsely settled and, except for hearsay reports from travellers such as Marco Polo and Ibn Batuta, were virtually unknown territory until, in 1723, Peter the Great laid the foundations of a town on the Iset River in the central Urals. The location of this community was chosen to guard the pass over the Urals and serve as an outpost for further expansion of the empire. The city was completed in 1726 (Cottrell, 1842) in the reign of Catherine I, and was named Ekaterinburg in her honour.<sup>1</sup> Ekaterinburg immediately became a centre for the copper mining industry, which had begun in 1701 and was controlled by the Demidoffs. Nearly all its inhabitants were either government officials or associated

<sup>1</sup> Екатеринбургъ, 56°52' N, 60°35' E; it is now called Sverdlovsk (Свердловск). Where possible, Russian localities are cited first in the author's spelling, then in the Cyrillic, and finally in modern English transliteration.



with mining. When J. G. Gmelin (1751) visited Ekaterinburg in 1733-34 it had a hospital and one wooden church. He made a trip to the copper works, about 52 versts away.<sup>1</sup>

Prospectors were soon to find the gold mines near Berezov<sup>2</sup> from which would come the first known lead chromates, but this had not happened before 1733-34, or surely Gmelin would have mentioned gold mines so close to Ekaterinburg where he was staying, particularly since he had a more than ordinary interest in mining. Reports of other, later visitors, particularly Peter Pallas, all tend to confirm that gold mining began after Gmelin's visit. When Pallas visited Ekaterinburg in 1770 it had grown considerably. There were two companies of soldiers and an artillery detachment quartered there, and there were stone churches and even a jail.

### CROCOITE

Some time between 1739 and 1766, in the gold mines near Berezov, the lovely orange mineral that is now called crocoite was found. It is strange that it was not reported until 1766, for it is strikingly beautiful and would immediately have aroused curiosity. The first report of its existence is probably that of J. G. Lehmann, who announced his discovery in a letter (in Latin) to Comte de Buffon on the 2 July, 1766. It is not certain that this letter was published. Dana (1951) cites: 'Nova minera plumbi (Lehmann, Nov. Comm. Ac. Petropol. 1766)', but there is no such paper in *Novi Comment. Acad. Sci. Imp. Petropol.*, 1766, vol. 10 (for 1764), in vol. 11 (1767, for 1765), in vol. 12 (1768, for 1766 and 1767), or in vol. 13 (1769, for 1768).

However, a German translation of the letter by Schulze appeared in 1767, and another independent German version in 1770 (Lehmann, 1767, 1770). In the 1767 version the title of the letter is quoted: *de nova minerae plumbi specie crystallina rubra*; and in 1769 B. G. Sage published a French version, using the name plomb rouge.

Lehmann stated that the new mineral had been discovered at a mine 'Pirosowka Sawod', 15 versts from Ekaterinburg,<sup>3</sup> and that the mineral had been mined with ores of copper, lead and silver. It occurred in cavities and interstices in quartz veins with altered pyrite and brilliant dendrites of a mineral resembling hematite. It might adhere to quartz, to iron or copper minerals, or even to galena. The form was lamellar or crystalline with a spathic texture. Crystals were four-sided. The colour was given as bright yellow-orange with a saffron streak. But crystals broken open might be the colour of Japanese cinnabar within.<sup>4</sup> Finally he mentioned its association with 'plomb blanche' (cerussite) and 'plomb verte' (pyromorphite).

Lehmann's chemical tests led him to believe that 'notre mine de plomb contient un spath séléniteux et du fer'. He looked for, but failed to find, sulphur, arsenic, cobalt, antimony, gold or silver. His analysis is incomplete, returning only 53.9%

<sup>1</sup> According to Kupffer (1833), a verst is 0.66288 miles; 1066.78075 metres.

<sup>2</sup> Березов (or Березовский, Berezovskii); 57°0' N, 60°50' E; commonly misspelt 'Beresov'. There are now several towns with similar or identical names in various parts of the U.S.S.R.

<sup>3</sup> The oldest mines in the Berezov district, eight versts from Berezov on the Pyshma River, would have been 15 versts from Ekaterinburg.

<sup>4</sup> Such crystals could not have been crocoite: they were probably phoenicochroite.



Pb. Exactly what Lehmann meant by 'spath séléniteux' is not clear. He may have considered it a sulphate; his test had shown only the absence of sulphide. No reference to selenium (discovered by Berzelius in 1817) can have been intended.

Lehmann checked the literature to see if others had previously found an orange or red lead mineral.<sup>1</sup> The ancients are in accord – they knew of no such mineral although they were familiar with artificial red lead oxides. Lazarus Ercker (1580, 1672; see also J. Pettus, 1683, and J. Justi, 1757) makes first mention of a red lead ore but said that it was clayey. J. G. Wallerius (1763) described a red lead ore as one stained with iron ochres.<sup>2</sup> M. V. Lomonosov (1763) mentioned bar-shaped or tabular red lead (with no silver content), but only in passing, and no locality was given. I find it hard to credit him with the discovery of crocoite as Hintze (1930) and Dana (1951) have done,<sup>3</sup> for surely he would have given more information on such an unusual new mineral. Dana credits him with giving Berezov as a locality but I have been unable to find mention of this. To add further doubt to these claims, Lomonosov said his red lead mineral occurred on fluorite gangue, a mineral I have not seen in suites of Berezov material, and which has not been noted by other authors.

P. Pallas, on his 1770 visit (Pallas, 1773 and 1794), is particularly helpful in the matter of date of discovery of crocoite. He visited the area near Totschilnaia-Gora,<sup>4</sup> where there was a sandstone quarry<sup>5</sup> that had passed into control of the Demidoffs in 1739. At several quarries in the vicinity, such as the Kouschvinskoi, he found crocoite<sup>6</sup> and at one he found 'fort belle mine de plomb blanc'. Pallas was also the first traveller to visit Berezov after Lehmann's announcement, and he paid attention to the mineralogy of the district. Although he saw specimens of the red lead ore from the mines he did not collect any. I. Lepechin (1775) also was a visitor in the summer of 1770 but had little interest in mineralogy.<sup>7</sup>

Pallas said that the gold mines were between the river at Berezov and the Pischma (= Pyshma) River, and were scattered over an area from one to eight versts from Berezov. The mines were near the village of Berezov and the Pyshma, Iset,<sup>8</sup> Néiva and Taguil (= Tagil) Rivers. There was yet another mine, 15 to 20 versts from Berezov on the Stanofka<sup>9</sup> River; it had produced gold from quartz veins like those at Berezov but they were lean and soon abandoned. The mines near the Pyshma were the oldest, dating back to 1745. The first of these was opened by eight shafts,

<sup>1</sup> Lehmann, incidentally, mentioned only white and green lead ores in his text of 1756.

<sup>2</sup> In his 1778 edition, he described Lehmann's mineral plumbi rubra, and clearly did not consider it the same as the ochre-stained red lead ores of the earlier edition.

<sup>3</sup> Hintze writes: 'Die erste Erwähnung des Rotbleierzses findet sich bei LOMONOSSOW (Grundlagen der Metallurgie, 1763, S. 44)'. The locality is not mentioned. Dana writes: 'Red lead-ore from Beresov. Lomonosov (*Grundlagen der Metallurgie*, 1, 44, 1763)'. 'Red lead-ore' is obviously a translation, but of what? Lehmann was either unaware of this mention or regarded it as another of the iron-stained ores mentioned by earlier authors.

<sup>4</sup> Точильная Гора, Tochil'naya Gora (the village of Точильная Ключ, Tochil'naya Klyuch, 57°29' N, 61°18' E, is 45 versts from Ekaterinburg).

<sup>5</sup> Pallas noted that some of these quarries had been worked centuries before.

<sup>6</sup> '... entre les fentes étroites de la pierre, beaucoup de cristaux plats de mine de plomb rouge. ...' He said the crystals were not very large, only up to an inch and a half long(!).

<sup>7</sup> He gives, however, an interesting account of the smelters, the mint and other activities in Ekaterinburg.

<sup>8</sup> Исет, 56°59' N, 60°23' E.

<sup>9</sup> Становая, Stanovaya, 56°52' N, 61°0' E.



but work was discontinued in 1765 because the gold ore pinched out with depth, another was being worked in a desultory way by unemployed miners, and a third was actively producing in 1770. Two other important mines were the Romanofskoi and Klioutschefskskoi.<sup>1</sup> The first of these was opened in 1762 by 14 shafts, but many of these shafts failed to penetrate the overlying gravels and many workings were in barren veins. The Klioutschefskskoi<sup>2</sup> opened a year later: it operated through 26 shafts with ten sumps and horse-operated pumps. It was a good producer but water seepage was a severe problem. Close to Berezov were four more mines, all in active production since 1752. These were the Numbers 6, 7, 12 and 24 or Perdounofskoi,<sup>3</sup> all near the river, with shafts from 30 to 60 feet deep, but flooding was no problem. Approximately 500 miners worked in the district and received from three to six kopeks per day depending on need and ability. The gangue was crushed and washed in mills near Berezov.

Pallas did little analytical work on crocoite. He found that it contained 43% lead, and yielded a little grain of silver, using crocoite from near Totschilnaia-Gora for his tests.

Crocoite, or plomb rouge, had a bad time of it at the hands of chemists and mineralogists for the three decades after its discovery by Lehmann. P. Davila & J. Romé de l'Isle (1767) described three fine specimens from 'Catherinebourg en Sibirie' but said that the mineral was lead mineralized with arsenic and sulphur. A little later (1772) Romé de l'Isle (who called the mineral 'plumbum hexaedrum rhombeum fulvum') said that it occurred with quartz, ores of iron and copper, and occasionally galena (Lehmann had already noted argentiferous galena as an impurity). A. G. Werner (1774) described the crystals as four-sided prisms (as seen in the collection of a Dr Schreber), but made no comment on the chemical composition.

B. G. Sage (1777) found 60 to 72% lead in plomb rouge<sup>4</sup> and called it an 'acide marin' with lead, coloured red by iron.<sup>5</sup> R. Kirwan (1784) misquoted Lehmann as demonstrating the presence of sulphur, arsenic and 34% lead in plomb rouge (Kirwan called it 'red lead spar') – an error that seems incomprehensible. But in most of Kirwan's works there is a misprint of 34 for 43% lead<sup>6</sup> (the correct value is given on p. 410 of the 1784 edition), and C. A. Hoffmann (1789, pp. 449, 473) took him to task for this error.

Louis Macquart travelled to Russia by order of the French Government in 1783 and obtained a considerable quantity of plomb rouge. He was given specimens by the Demidoffs and Prince Scherebatoff, and bought other pieces in St Petersburg. In 1789 he correctly quoted Lehmann's chemical results and made the helpful observation that Lehmann must have considered the mineral to be a 'chaux' (i.e. a calx or oxide) of iron and lead (Macquart, 1789). Evidently, to Macquart 'spath séléniteux' had no special implication as to radicals in the mineral. Upon his return

<sup>1</sup> These are adjectival forms, from Романов, Romanov, and Ключ, Klyuch.

<sup>2</sup> Pallas says: 'On m'a assuré qu'il existoit, au fond de la mine de Klioutschefskskoi, une masse énorme de topaz . . . .'

<sup>3</sup> An adjectival form from Пердунув, Perdunov.

<sup>4</sup>  $\text{PbCrO}_4$  contains 64.11% Pb.

<sup>5</sup> Noted by Monnet (1779) who points out that Siberian plomb rouge differed from flesh-coloured lead ores from Poullaouen and Valgouet.

<sup>6</sup> Presumably, but not certainly a citation of Pallas' determination.



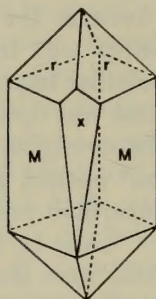


FIG. 1. Crocoite, Berezov ; after Haüy, 1801.

to France he gave the crystalline material to René Just Haüy for study. Haüy recognized two habits characterized by elongation in two possible directions, and some of his crystal drawings are figured in his *Traité* (1801). The largest crystals were 10–12 lignes<sup>1</sup> long and were loosely attached to their quartz gangue.

Macquart also described the associated species on these specimens. One of these was probably vauquelinite (see later). Another was a crystalline mineral that had the colour of native sulphur. This was probably cerussite stained with chromates. Another yellow mineral, in slender needles, was probably vanadinite or pyromorphite. And what Macquart described as 'oxide jaune ou ocre de plomb' (seen on specimen No. 24, misprinted 34) was possibly embreyite.

Assisted by L. N. Vauquelin, Macquart (1789) attempted an analysis of plomb rouge and obtained: Pb 36 $\frac{1}{9}$ %, O 37 $\frac{5}{9}$ , Fe 24 $\frac{8}{9}$ , alumina 2 (totalling 100 $\frac{5}{9}$ %) ; the excess he attributed to moisture in his precipitates.<sup>2</sup>

Macquart discussed the use of pulverized plomb rouge as an orange pigment for painters, noting that it should be superior to arsenic sulphides, which tended to darken in the French climate. E. M. L. Patrin, who visited Berezov in 1786, was concerned about the supply of pigment from the mines. The best vein of crocoite had pinched down to the width of two pous<sup>3</sup> by this time, and no good material had been found for 15 years. As the supply of the mines dwindled, the price of specimens soared, and Soret (1818) mentioned that 'D'immenses druses, provenant du cabinet de Sitnikoff, ont été bocardées pour cet usage [as a pigment for ceramics] ; plus les cristaux sont nets et transparents, plus ils sont recherchés'.

B. F. J. Hermann (1789) visited Berezov at about the same time as Macquart. He placed the time of first mining there at 1744, and milling began in 1752 – a date matching that given in Rose's (1837) production tables. Hermann performed some chemical tests on plomb rouge and cited Lehmann's analysis of about 50% lead plus iron, but said it also contained silver and carbonate. He called the mineral 'Minera plumbi spathosa', and referred to additional occurrences at Totschilnaja Gora (Tochil'naya Gora) and at Poelstaja Prepost near Ui.<sup>4</sup>

<sup>1</sup> A ligne is 2.12 to 2.26 mm.

<sup>2</sup> i.e. he found 13 grains of lead in 36 grains of sample, hence the peculiar fraction.

<sup>3</sup> A pousse (inch) is 25.40 to 27.07 mm.

<sup>4</sup> Poelstaja Prepost was not located; the River Ui (Уи, Ui) is south of Sverdlovsk, and a portion of its course is the boundary between the Chelyabinsk Oblast and Kazakhstan.



I. von Born (1790) and J. F. Gmelin (1790) were the first to mention crocoite localities outside Siberia. Born's locality was Reczbanya<sup>1</sup> in Hungary. Gmelin grouped all red lead ores together as one species, but doubtless only red lead from Berezov was crocoite. T. Bergmann *et al.* (1792) gave little data in their text. They cited a prism angle of  $62^\circ$  (Haüy in Macquart, 1789, had given  $60^\circ$ ), and they referred only to Macquart's analysis. The mineral was called 'plomb mineralisé par l'air pur' (i.e. oxygen).

J. J. Bindheim (1792) in Moscow seriously questioned the older analyses. He examined crocoite ('sibirischer rother bleyspat') and determined a specific gravity of 5.750.<sup>2</sup> The first determination had been made by M. Brisson (1787) who obtained 6.0269. Bindheim's chemical analysis gave: 'hergestelltes Bley 60%, Molybdansäure 11 $\frac{2}{3}$ %, Nickelkalk (mit Inbegriff des geringen Gehalts von Kobold und Kupffer . . .) 5 $\frac{2}{3}$ %, Eisenerde 1%, luftleere Kalkerde 6%, Kieselerde 4 $\frac{1}{2}$ %, flüchtige Bestandteile 5%, Verlust 6 $\frac{1}{8}$ %'. Bindheim doubted von Born's report of crocoite from Retzbanya, and thought it must be a different mineral.

By now the authors of mineralogical texts were, understandably, confused. How could chemists such as Lehmann, Macquart and Bindheim disagree so completely? All agreed only upon the fact that the mineral contained lead. Kirwan (1796), for example, cited both Bindheim and Macquart and, forced to choose, sided with Bindheim. He also reported (p. 214) that 'In France it is said to have been found massive, but more generally disseminated or overlaying'; but no French authors have mentioned this.

The problem was to be resolved by N. L. Vauquelin who made a remarkable discovery. Vauquelin had worked as an assistant to Macquart and was not satisfied with their analysis. In 1797 he stated that he had come to believe that plomb rouge contained neither molybdenum, cobalt, nickel and copper (according to Bindheim) nor iron and aluminium as Macquart and he had earlier found. Vauquelin even said that he and Macquart had searched in vain for Lehmann's arsenic! This is a surprising statement because Lehmann also had sought it in vain and Macquart correctly quoted Lehmann as failing to find it.

Vauquelin's experiences with plomb rouge indicated to him that it contained a new metal and lead only (and oxygen, of course). The metal present gave a variety of colours to its salts so he called it chrôme<sup>3</sup> following a suggestion by R. J. Haüy; elsewhere (*Crells Chem. Annln*, 1798) he credited both Haüy and A. F. de Fourcroy with the suggested name. He also synthesized crocoite by mixing potassium chromate (obtained in the course of his analysis) and lead nitrate solutions and his analyses of the natural and artificial material are: natural, PbO 63.6%, CrO<sub>3</sub> 36.4 (by difference);<sup>4</sup> synthetic, PbO 65.12%, CrO<sub>3</sub> 34.88 (by difference).

His discoveries were widely published, with first notices considerably earlier than the dates of 1797 or 1798 given by many writers. The first notice appeared in 1794

<sup>1</sup> Retzbanya, Rézbánya, now Baita, distr. Bihor, Romania,  $46^\circ 29' N$ ,  $22^\circ 38' E$ .

<sup>2</sup> In Kirwan's 1796 edition this is misprinted as 5.50 but was corrected in later editions.

<sup>3</sup> *Chromium* first appears in D. Reinecke's translation (*Crells Chem. Annln*, 1: 183 (1798)).

<sup>4</sup> This analysis has been mistakenly referred to Thénard by Jameson (1837) and Phillips (1823). In the most widely quoted version of Vauquelin's results (*J. Mines, Paris*, 1797) the analysis for PbO is misprinted as 63.96% on p. 760 and 6.86% on p. 744. These misprints have been faithfully copied elsewhere, e.g. in *Crells Chem. Annln*, 1798; Suckow (1804) explains the 6.86% as 'Sauerstoff', giving 57.10% 'Blei', 36.04% 'Chromsäure'.

with a note, added in proof, that he had just succeeded in isolating the metal.<sup>1</sup> The name *chrôme* appeared in 1796. Vauquelin also observed that only crystal fragments or broken specimens were pulverized for pigment: the good pieces, he said, adorned mineralogical cabinets throughout the world.

Vauquelin's discovery was generally accepted by the scientific community, but there were a few notes of discord. M. Klaproth (1798) lamented that he had not had enough material to name the new metal since his experiments had led him to believe that crocoite contained one; as a result, some later writers have cited Klaproth as co-discoverer (Partington, 1962). More amusing was a blast by Sage (1800) citing a fictitious analysis by Vauquelin (neither Thénard<sup>2</sup> nor I could find it) given as: plomb 36%, acide chromique 37, fer 24, alumine 2. This analysis shows suspicious similarities to Macquart's except that 'acide chromique' replaces oxygen. Sage then proceeded to present his 'correct' analysis: antimoine 45% (actually 'par quintal'), chrome, plomb and alumine ('N'ayant pu séparer avec précision le plomb, je ne précise que la quantité d'antimoine'). L. S. Thénard (1800) immediately responded with a vigorous and amusing defence of Vauquelin. He extended himself very far, however, to show that Sage's material was contaminated with gangue,<sup>3</sup> for he presented an analysis of gangue showing 19% Sb<sub>2</sub>O<sub>5</sub>. Stibnite does occur at Berezov but is rare, and it is almost inconceivable that Sage could find 45% Sb and not notice stibnite as the impurity. Thénard then analysed crocoite, using Vauquelin's procedure, and found: PbO 64%, CrO<sub>3</sub> 36.

#### VANADIUM MISTAKENLY IDENTIFIED AS CHROMIUM

In Mexico, A. Del Rio (1804) had a brown lead mineral from Zimapan, which he rightly thought contained a new element. He planned to call the element *panchromium*, then *erythronium*,<sup>4</sup> and his analysis showed 80.72% PbO and 14.8% erythronium but when he heard of Vauquelin's discovery he thought it might be chromium instead.<sup>5</sup> He sent some material to Humboldt in Paris but the ship sank, and Humboldt's own specimens (brought back by him earlier) found their way to H. V. Collet-Descotils (1804-5) who published an analysis:<sup>6</sup> 'plomb métallique 69%, oxigène présumé 5.2%, oxide de fer insoluble dans l'acide nitrique 3.5%, acide muriatique sec 1.5%, acide chrômique 16%, perte 4.8%'. J. C. Delamétherie (1806) later said: 'Delrio, savant minéralogiste de Mexico, avoit soupçonné que cette mine contenoit un nouveau metal. Sans doute sera le chrôme qui l'aura induit en erreur.' Del Rio gave up and lost his chance to discover vanadium. His specimens found their way to the Museum für Naturkunde in Berlin, where Humboldt's labels were corrected in Rose's handwriting to 'vanadium Bleierz' some 30 years later (Weeks, 1935). But some writers continued to cite the original analysis, and listed

<sup>1</sup> From the description, it was probably one of the chromium carbides.

<sup>2</sup> Thénard: 'Où le citoyen Sage a-t-il pu puiser cette analyse si fausse du plomb rouge, qu'il attribue si légèrement au cit. Vauquelin?'

<sup>3</sup> Elsewhere he said that Sage probably confounded muriate of lead with muriate of antimony.

<sup>4</sup> See also Humboldt (1804): 'In dem braunen Blei von Zimapan hat Herr Delrio . . . ein von chromium . . . sehr verschiedenes Metall entdeckt, welches er für neues hält, und . . . Erithronium gennant hat'.

<sup>5</sup> Del Rio (1804): 'pero habiendo visto en Fourcroy que el acido crómico da tambien por evaporación sales roxas y amarillas creo que él plomo pardo es un cromato de plomo . . . ser'; see also Del Rio (1822).

<sup>6</sup> Misprinted in part in Eschwege (1820).



the mineral as a chromate long after this (Dufrénoy, 1856). Wöhler re-examined the Zimapan mineral, and recognized that it contained the metal then newly discovered in Taberg iron by Sefström (postscript by P. [Poggendorff] to Sefström's paper, 1831). In 1833 Rose showed that Berezov 'braunes Bleierz' was identical with the Zimapan mineral, which Kobell (1838) later named vanadinite.

#### LATER OBSERVATIONS ON CROCOITE

J. B. Richter (1800) published another early analysis of crocoite. This has been virtually forgotten and I have seen it referred to only in Klaproth and Wolff (1807). His analysis is: PbO 72.3%, CrO<sub>3</sub> 27.7. The analysis appears to have been carefully done; chromate was weighed as the green oxide (Cr<sub>2</sub>O<sub>3</sub>). C. H. Pfaff (1816) published an analysis giving: PbO 67.9125%, CrO<sub>3</sub> 31.725 (totalling 99.6375) and two years later J. J. Berzelius published two analyses: crocoite, PbO 68.50%, green chrome oxide 24.14, oxygen lost (calc.) 7.56 (totalling 100.00); synthetic, PbO 68.259% and CrO<sub>3</sub> 31.761. The method of his synthesis was that of Vauquelin.

B. F. J. Hermann (1803, 1804) added some interesting notes on the Berezov locality as it was in about 1800. He described branching or arborescent gold specimens several inches long, but said that they had not been found for some time. He also noted that no new localities for chromates had been found recently and that in the mines where they did occur pods of galena rimmed with chromates were only occasionally encountered. Haüy also gave some notes of interest in the 1801 edition of his *Traité*. He said that the chromates were worked out about 1760 (undoubtedly an error – Patrin's approximate date of 1771 is far more likely) and that some good crystals had later been found in isolated pockets together with clay. The veins ran north-south, parallel to the banding in the quartz-mica-schist wallrock and also carried wulfenite, pyromorphite and anglesite. His crystallographic observations then led him to the conclusion that the base of the primitive form of crocoite was normal to the prism. In 1809 he said that the base was inclined 'some degrees' to the prism, and in 1822 he gave  $\beta$  as 103°16'. In this later work he also told of a mine official who sold a specimen for its weight in Russian coinage, an equivalent of 680 francs. Truly, as he said, 'le plomb rouge se vend très cher, même en Sibérie'.

Wiedemann (1801) described a specimen in Villier's collection in Metz, which was 1½ Fuss across with crystals 2 to 2½ Zoll long and ½ Zoll thick.<sup>1</sup> It was also coated in places with 'the usual red, yellow, and green minerals'. What has become of this fabulous specimen is not known.

Vauquelin evidently had a keen eye on the commercial value of synthetic lead chromate as a pigment, for he mentioned his hope of finding some more common chromium mineral. This was very soon realized by the discovery in 1797 in Var, France, of chromite. This was first analysed by F. Tassaert (1797),<sup>2</sup> who gave it to Vauquelin, who reanalysed it. Later, chromite was found in Siberia and analysed by A. Laugier (1811).

<sup>1</sup> A Fuss is about a foot, a Zoll about an inch.

<sup>2</sup> Not by Vauquelin, who usually is given the credit, as by A. F. Silvestre (1799), for example.

Vauquelin (1809) experimented with the colours of chromates of lead precipitated from neutral, acid and alkaline solutions. He noted that alkaline solutions gave the reddest precipitates and also observed that an excess of lead oxide in lead chromate gave richer reds. These prophetic observations were soon followed by a paper by P. L. Dulong (1812) who boiled a solution of potassium chromate and lead carbonate and obtained a rich red precipitate that in nitric acid turned yellow 'en cédant oxyde de plomb'.

J. F. L. Hausmann (1813) called crocoite 'Kallochrom' and gave a very interesting account of the Berezov chromates. Most important are his remarks on one species that he observed; '... ein anderes Mineral vor [kommt], welches nach meinen Versuchen chromsaures Blei zu enthalten scheint und eine genauere chemische Untersuchung verdient. Es ist theils dunkel ocherbraun, theils dunkel leberbraun; giebt aber ein zeisiggrünes Pulver. Im Bruche eben, einer Seits in das Flachmuschliche, ...' This is the first clear description of embreyite. This description was read with interest by Ullman (1814), who described his collection of specimens in great detail. Some of these clearly contained not only vauquelinite but phoenicochroite.

J. L. De Bournon (1813) disagreed with Haüy's early crystallographic data for crocoite, stating that the primitive form is a prism with angles about  $85^\circ$  and  $\beta$  about  $108^\circ$ . Probably his crystals were of totally different habit. F. Soret (1818, 1820) added new forms to the list for crocoite and in 1818 described the primitive

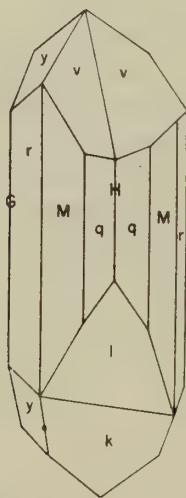


FIG. 2. Crocoite, Berezov; after Soret, 1818.

form as having  $\beta$   $102^\circ 51'$  and a prism angle of  $91^\circ 27'$ ; in 1820 he gave  $\beta$   $103^\circ 16'$  and a prism angle of  $93^\circ$ . His specimens were obtained from M. Duval, 'Consul général de la Confédération Helvétique, en Russie' and M. Jurine. H. Dauber (1859, 1860) gave crystallographic data for crocoite that have been widely cited.



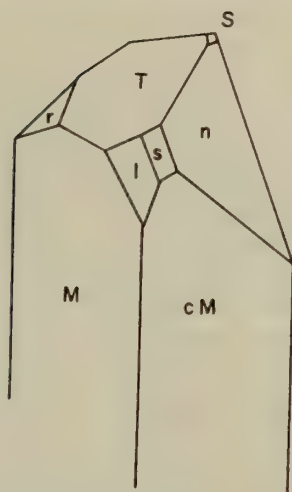


FIG. 3. Crocoite, Beresov ; after Kupffer, 1827.

He measured crystals from Brazil and the Philippines as well as from Berezov. Some fine drawings are presented in his 1860 paper.

J. C. L. Zincken (*in* W. L. Eschwege, 1820) described a new occurrence of crocoite in Brazil. He described one specimen of 36 square Zoll with crocoite crystals (of '... mittlerer Grosse, klein und sehr klein') scattered on sandstone. The crystals were partly covered with earthy pyromorphite. The locality given was Conconhas do Campo.

F. Mohs (1824) in his *Grundriss der Mineralogie* listed crocoite as 'hemiprismatischer Blei-Baryt'. He cited Pfaff's analysis and gave a specific gravity of 6.004 for Siberian material. This value was determined and published later by W. Haidinger (1825) and must have been previously communicated to Mohs. In 1827 A. T. Kupffer presented new measurements for crocoite, including a prism angle of  $93^{\circ}44'$ , with one crystal drawing. He had been to the Urals (1829) and discussed the geology of the range in some detail. He had also described visits to the Berezov gold mines but never mentioned chromates. He did note, however, that the largest gold nugget found to date weighed 26 pounds.

A. Wehrle (1832) reported the occurrence of crocoite ('hemi-prismatisch Bleibaryte') at Retzbanya, as von Born had done more than 40 years before ; he was unaware of von Born's paper as well as of the fact that Bindheim had been doubtful of von Born's identification. Despite the confident sound of the title of his paper, Wehrle admitted that he did not know whether the Retzbanya mineral was crocoite or vanadinite.

F. S. Beudant (1832) proposed the name crocoïse from the Greek *κροκοεις*, 'jaune aurore' ; F. von Kobell (1838) modified this to Crocoisit, and A. Breithaupt (1841) to Krokoit, and which is the name generally in use in Germany. J. D. Dana (1868) appears to have been the first to use the form crocoite, now usual in English-speaking countries and which he derived from *κροκος*, saffron. H. Brooke and

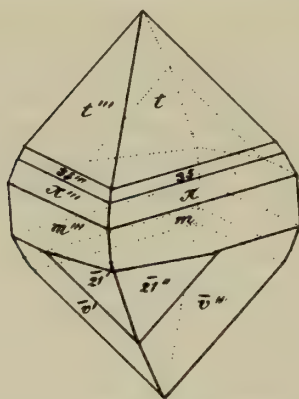


FIG. 4. Crocoite, Philippines ; after Dauber, 1860.

W. H. Miller (1852) proposed the name *lehmannite* in honour of J. G. Lehmann, but this name has never gained currency.

C. Baerwald (1882) published the first new analysis of Berezov crocoite in over 60 years. Determinations of the optical properties were included in the same paper. Baerwald used a specimen borrowed from C. F. M. Websky for this work. His analysis was :  $\text{PbO}$  68.82%,  $\text{CrO}_3$  31.16, totalling 99.98.

A. Liversidge (1895) provides the first analysis of Tasmanian crocoite :  $\text{PbO}$  66.86%,  $\text{CrO}_3$  30.99,  $\text{Fe}_2\text{O}_3$  1.02, totalling 98.87 ; sp. gr. 5.92. The crocoite discoveries at Dundas, Tasmania, had just been made and several mines were producing the superb specimens that are now to be found in mineralogical cabinets throughout the world. These occurrences have been described in a series of publications by W. Petterd (1893, 1896, 1901, 1902, 1903, 1910), and the morphology of the Dundas crocoites has been described by Palache (1896) and Anderson (1906). In 1931 R. Brill published cell constants for crocoite,  $a$  7.10 kX,  $b$  7.40,  $c$  6.80, and accepted the morphologically determined angle  $\beta$  as  $102^\circ 27'$ . Later, S. Gliszczynski (1939) demonstrated the similarity of monazite and crocoite and gave :  $a$  7.108 kX,  $b$  7.410,  $c$  6.771,  $\beta$   $103^\circ 37.9'$ .

Y. Laurent *et al.* (1967) described an occurrence of crocoite from central France near Nontron. A new chemical analysis was given together with morphological data. Very fine but small crystals were found here associated with pyromorphite. They did not say if the locality could be the same as that mentioned long before by Kirwan (1796).

#### VAUQUELINITE

Macquart (1789) described the minerals accompanying crocoite (*plomb rouge*) ; pyromorphite crystals of clearly hexagonal outline up to four lignes long were common. Another green mineral (elsewhere described as black or blackish green) occurred in small cuneiform crystals. This was unquestionably the first notice of vauquelinite, and Macquart believed he was seeing the mineral described earlier by Lehmann as a dark mineral – '*ressemblans à une mine de manganèse venue*



d'Orientbourg'. I doubt this identity and believe Macquart alone should be credited with the first mention of vauquelinite. Macquart's specimens nos. 26 and 31 ('plomb noir') fit vauquelinite well; so do nos. 31, 32 and 33 ('plomb vert noirâtre cunéiforme'). His tests (*Essais*, p. 357) showed him that the latter contained less than half as much lead as plomb rouge, and that it contained iron.

Berzelius (1818) named this second mineral of lead and chromate vauquelinite.<sup>1</sup> His analysis was: CuO 10.80%, PbO 60.87, CrO<sub>3</sub> 28.33. As will be seen later, the analysis was faulty, but the mineral is nevertheless a valid species. Mohs (1824) later gave a specific gravity of between 6.8 and 7.2 and noted that the mineral also occurred in Brazil. F. von Kobell (1838) inadvertently hinted at future problems of identity when he described vauquelinite as sometimes occurring in needles or spear-shaped crystals. These would certainly be pyromorphite, and the inability of some mineralogists to distinguish between these two green minerals was to lead to a number of suspect analyses of vauquelinite. To increase the difficulty, these two minerals may occur intimately mixed at Berezov, and G. Rose (1839) was satisfied that the CrO<sub>3</sub> he found in an analysis of pyromorphite (Berezov material) was due to contamination.

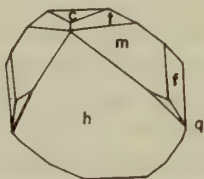


FIG. 5. Vauquelinite, Arizona.

J. John (1845) described a new mineral, 'Chromphosphorkupferbleispath,' a pistachio green to olive brown, fine-grained mineral from Berezov, giving an analysis: 'chromsäures Blei 45%, Bleioxyd 19.0%, Kupferoxyd 11.20%, Phosphorsäure 4.10%, Chromsäure mit Spuren Mangans 7.50%, Wasser 1.78%, schwarzbraunes, noch näher zu bestimmendes Oxyd [und] weisses, metallisches Oxyd 11.42%' (totalling 100.00%). As recognized by Dana (1868), it was probably an impure vauquelinite.

John had purchased some specimens of Berezov material in Berlin, and his description of one of the associated minerals is of even greater interest. He wondered if it could be vauquelinite but wrote: 'Ein nelken- und haarbraunes Erz in dünnen amorphen Massen; matt und wachsartig glänzend, undurchsichtig und kaum an dünnen Kanten durchscheinend; von zeisiggrünem Striche'. This was undoubtedly impure embreyite (Williams, 1972).

In 1867 (again in 1869) A. Nordenskiöld described as new a mineral from Berezov and named it laxmannite. He was well aware of its similarity to Berzelius' vauquelinite, but maintained that Berzelius had only given an incomplete description of pseudomorphs (of what after what he did not say). He did not believe that vauquelinite was invalid, however, but that it should stand in isomorphous relationship

<sup>1</sup> He was by no means the first to notice it. After Macquart (1789) it is mentioned by Meder (1799), Vauquelin (1801), Ludloff (1804), Thompson (cited by Delamétherie, 1806), and finally Ullmann (1814) who described it well but stopped short of naming it. Ludloff's description is most unconvincing.

to laxmannite by phosphate-chromate substitution. His two analyses of laxmannite were: PbO 61.26%, 61.06; CuO 12.43, 10.85; Fe<sub>2</sub>O<sub>3</sub> 1.09, 1.28; CrO<sub>3</sub> 15.26, 16.76; P<sub>2</sub>O<sub>5</sub> 8.05, 8.57; H<sub>2</sub>O 1.31, 0.90 (totalling 99.40 and 99.42). Nordenskiöld gave morphological data<sup>1</sup> together with a crystal drawing. The mineral was dark olive to pistachio green.

When H. R. Hermann (1870) noticed this new description he asserted, with justification, that Berzelius had probably overlooked the presence of phosphate in his precipitate and calculated it all as chromate.<sup>2</sup> Hermann recalculated Berzelius' analysis in such a way that it became identical to laxmannite, thereby discrediting the latter species. He filled the newly created gap with his own new species, phosphorchromite. For this he gave a specific gravity of 5.80. The mineral occurred on Berezov specimens as nodules with a partly crystalline dense greenish black core overgrown with small dark crystals for which no morphological data were given. I have seen a number of specimens fitting this description in the British Museum (Natural History) collection, e.g. BM 40448. Hermann's analysis was: PbO 68.33%, CuO 7.36, Fe<sub>2</sub>O<sub>3</sub> 2.80, CrO<sub>3</sub> 10.13, P<sub>2</sub>O<sub>5</sub> 9.94, H<sub>2</sub>O 1.16, total 99.72. This material is doubtless a mixture of vauquelinite and the massive unidentified material recently described with embreyite (Williams, 1972).

N. I. Koksharov (Кокшаров, Kokscharow), formerly inspector of mines at Berezov, published (between 1853 and 1888) an important series of volumes on the mineralogy of Russia. The Berezov chromates are covered exhaustively in volumes 4 (1862), 6 (1870), 7 (1875) and 8 (1878). Interfacial angles determined by others for crocoite and vauquelinite are tabulated along with new measurements by Koksharov. He later came to believe that the chromphosphorkupferbleierz (of John) and phosphorchromite (of Hermann) were near vauquelinite although in an earlier volume he had reported laxmannite and phosphorchromite with almost eerie detachment, totally ignoring Hermann's arguments. A new analysis by Nicolajew was given for vauquelinite: PbO 62.70%, CuO 9.58, CrO<sub>3</sub> 11.95, P<sub>2</sub>O<sub>5</sub> 9.23, volatiles 3.00, totalling 96.46. A new specific gravity of 6.06 was also reported.

Koksharov and Des Cloizeaux (1882) gave morphological arguments to show that laxmannite was vauquelinite. They also relegated J. John's chromphosphorkupferbleispath and H. R. Hermann's phosphorchromite to synonymy. This view has persisted up to the present without being seriously questioned, and the problems that began with von Kobell's identification of needles or spear-shaped crystals (actually pyromorphite) as vauquelinite seem to be completely smoothed out.

#### PHOENICOCHROITE

J. Badams (1825) credited Dulong (1812) with the first mention<sup>3</sup> of another, dark red, synthetic lead chromate, and tried to follow Grouvelle's (1821) recipe for

<sup>1</sup> Dana (1951, vol. 2, p. 652), quoting these, says 'Orientation and axes of Nordenskiöld'. This is not strictly true: Nordenskiöld used a setting with  $a[100]$  as symmetry axis, and his  $a$  and  $b$  axes have been interchanged.

<sup>2</sup> Berzelius precipitated the filtrate from the separation of lead and copper, containing the chromium as Cr<sup>3+</sup>, with ammonia, and ignited and weighed the precipitate, reporting it as Cr<sub>2</sub>O<sub>3</sub>. It would have contained most if not all of the P<sub>2</sub>O<sub>5</sub> present.

<sup>3</sup> Actually, the first mention of a distinct dark red lead chromate was by Vauquelin, in 1809; but see Lehmann, 1766, under crocoite (p. 381, footnote 4).



its preparation. He managed to get a 'scarlet sub-chromate of lead' by these means and analysed the product to assure himself that it contained no potassium. His analysis gave:  $\text{PbO}$  38.40%,  $\text{PbCrO}_4$  60.0. P. Grouvelle's method involved the warming of lead chromate in a slightly alkaline solution with or without the addition of litharge. Grouvelle had not analysed his product but Badams studied the process more carefully in hopes of creating a new red pigment. J. Liebig and F. Wöhler (1831) prepared a basic lead chromate by fusing lead chromate in potassium nitrate. The product, after gentle washing by decantation, gave a red salt assumed to be basic, but no effort was made to identify or analyse it.

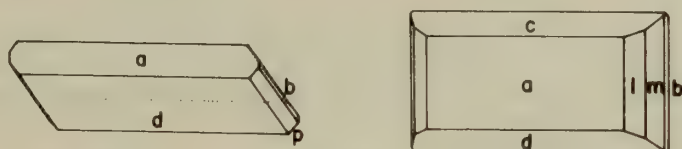


FIG. 6. Phenicochroite, Arizona; after Williams *et al.*, 1970.

In 1833 H. R. Hermann described a third new lead chromate from Berezov. It is barely possible that it had been artificially created by the workers described above. Hermann named the mineral melanochroite because, although red, it was notably darker than crocoite. He discovered the species on five specimens in a collection of 40 pieces of chromate ore from Berezov. His analysis<sup>1</sup> gave:  $\text{PbO}$  76.69%,  $\text{CrO}_3$  by difference. The mineral was of tabular habit with two good cleavages and a specific gravity of 5.75. E. F. Glocker (1839) used the name Phönikochroit (meaning dark red colour) to replace melanochroite since, strictly speaking, melanochroite implies black. Hermann, of course, used the name in the sense, dark coloured. Two years later A. Breithaupt (1841) proposed the name Phönicit (short for phönicitus plumbosus) but this name was objectionable owing to its similarity to phenacite, a beryllium mineral named in 1833. W. Haidinger (1845) used the name Phönicit in his *Handbuch*, and is usually, and erroneously, given credit for proposing it. H. Brooke & W. Miller (1852) used phoenicite for phenicochroite, as did A. Kennigott, but this name was soon to die out. Phenicochroite has best withstood the test of time and is generally accepted today.

G. Rose (1837) published an important work on Berezov, which was based on his experiences while travelling with A. von Humboldt and Moritz von Engelhardt. His observations on the Urals in the vicinity of Berezov comprise the first coherent report on the geological setting. And he gave the first clear account of some of the associated minerals such as aikinite<sup>2</sup> (with an analysis by his brother Heinrich), tetrahedrite, dolomite, pyrite and crystalline gold. Analyses of gold are presented with complete production figures dating back to 1754. His observations on the

<sup>1</sup> Using a method likely to lose some Pb as soluble  $\text{PbCl}_2$ , M. H. Hey, pers. comm., 1971.

<sup>2</sup> A specimen of 'aikinite' from Berezov (BM 57624) was analysed in duplicate by M. Duggan (Phelps Dodge Corporation) and gave Bi 56.0%, 55.8, Pb 18.7, 18.8, Cu 5.85, 5.74; this corresponds to a formula  $\text{CuPbBi}_3\text{S}_6$ , and the material may be lindströmite.

three lead chromates found there – crocoite, vauquelinite and melanochroite – are accurate but add little to the growing list of physical and chemical data being amassed by his contemporaries. He did, however, make some useful observations. He noted that until H. R. Hermann described melanochroite, it had been confounded with crocoite ('rothbleierz'). As we have seen (this paper, p. 381, footnote 4), this confusion probably began with Lehmann, thus giving melanochroite an antiquity equal to that of crocoite. Another comment, one I have seen nowhere else in the old literature, was that melanochroite tended to cleave at right angles to its plane of flattening. This is true, and would serve modern workers in its identification. Rose did not mention mine no. 7, which had long since been exhausted. He stated that most chromates were being found at the Preobraschenski (Preobrazhenski) mine, but its production was small in comparison with the older mines. Melanochroite and vauquelinite, as well as crocoite, were found there but were rare: the best vauquelinite locality was then the Zwetnoi (Tsvetnoi) mine, a locality I have seen mentioned by nobody else.

W. F. Petterd (1895) described phoenicochroite from Tasmania, under the old name melanochroite. It occurred as small dark red 'amorphous' masses on gossan, found at the Adelaide Proprietary mine.

A. K. Temple (1956) reported finding phoenicochroite in the Hopeful vein at Leadhills, Scotland, and based his identification on the similarity of its X-ray powder pattern with that of a specimen of Berezov material labelled as phoenicochroite at the British Museum (Natural History); his specimen (one of two) occurred as massive red material with cerussite and leadhillite. Contamination with cerussite is to be expected in this association, and comparison of the X-ray powder pattern with that of pure phoenicochroite confirms that both his specimen and the comparison specimen are impure phoenicochroite, a conclusion that has Dr Temple's agreement.

Temple also described a chromian leadhillite with about 0.5% Cr (determined spectrographically). Most interesting, however, was his partial description of a possible (and unnamed) new mineral which was a 'chromian lanarkite'. This was found at the Hopeful vein also, as small, elongated bright red crystals with cerussite. Spectrographic analysis showed 6 to 15% Cr by weight, and complete X-ray powder data were given. If his mineral had no more than 7.2% Cr it would be phoenicochroite with no room left for  $\text{SO}_4$ . The X-ray powder data fit phoenicochroite nicely (see Appendix) and show no signs of contamination. I am reasonably certain that Temple's 'phoenicochroite' was impure phoenicochroite, and his 'new mineral' was pure phoenicochroite.

P. Bariand & P. Herpin (1962) found phoenicochroite at Sebarz Anarak, Iran, with fornacite, iranite (see below), diopase, diaboileite, etc. (see also Bariand, 1963). Unfortunately a modern definition of phoenicochroite by Bariand was refused by the French Nomenclature Committee on the grounds that his material was not adequately tied to type material. This decision was to cause more problems within the next decade.

D. Adib & J. Ottemann (1970) published a scanty description of a new mineral they had found in Iran. This was a red lead chromate to which they assigned the

formula  $\text{PbCrO}_4\text{PbO}$  and named chrominium. Incorrect cell constants were presented without supporting powder data, and no consideration was given to other lead chromates.

Shortly afterwards A. Mücke (1970) described another 'new' lead chromate (scheibeite) from Sierra Gorda, Chile. An analysis of synthetic material was given, after showing by comparison of X-ray powder diffraction data that this product was identical to the new mineral. X-ray unit cell data were also presented and compared with Bariand and Herpin's and Adib and Ottemann's results. Despite the obvious similarities, Mücke put his faith in the analysis (which gave  $\text{Pb}_8(\text{CrO}_4)_3\text{O}_5$ ) and proceeded with the description of what he thought was a new mineral.

In 1970, I published, with J. McLean and J. W. Anthony, a redefinition of phoenicochroite. This material had been found in Arizona with other chromates, perhaps at the locality B. Silliman, Jr, meant in 1881 (see p. 399). Our data were essentially in agreement with those in Bariand's unpublished manuscript, and we had no reason to believe that it was not identical to Hermann's phoenicochroite. No specimens from Berezov had been found, nor have they since, that failed to match the meagre description by H. R. Hermann, nor has more than one species of dark red colour been observed in Berezov material. Like Bariand, we saw no reason to question the identity of Berezov phoenicochroite. Later in the same year, J. Zemmann (1970) obtained Mücke's X-ray powder photographs and specimens of Adib and Ottemann's chrominium. He took his own photographs and found that they matched not only each other but our data for phoenicochroite as well. A recent vote by the New Minerals Commission of the International Mineralogical Association on this matter has settled the question, reaffirming phoenicochroite as the acceptable name for this species.

#### SYNTHESES—REAL OR SUPPOSED—OF PHOENICOCHROITE AND OF OTHER BASIC LEAD CHROMATES

Many authors besides Grouvelle (1821), Badams (1825) and Liebig & Wohler (1833) have described the preparation of red, basic lead chromates but in most cases there is no evidence that the product was homogeneous and in many, no chemical analysis.

N. C. Manross (1852) obtained ruby-red crystals 'viel zu dunkel für neutrales chromsäures Blei', which he thought were phoenicochroite, by fusion of lead chloride and potassium chromate. He gave a specific gravity of 6.118 for his product but no analysis was offered. However, he observed crystals of (pseudo)<sup>1</sup> hexagonal habit with a prism angle of  $119^\circ 54'$ . A. Drevermann (1853, 1854) claimed to have synthesized phoenicochroite and crocoite by diffusion in water between vessels containing solutions of potassium chromate and lead nitrate. No evidence was offered. Phoenicochroite was supposed to have formed as small, dark red rhombic tablets, crocoite as needles three to four millimetres long. A. Becquerel (1866) claimed that he grew phoenicochroite and crocoite using slightly different electrolytic methods. Only the colour of the products was cited as evidence. S. Meunier (1878) reported a simple procedure for producing phoenicochroite. He had used

<sup>1</sup> i.e. he said they were hexagonal but this is contradicted by the prism angle he cited.



this method successfully to produce brochantite and A. Des Cloizeaux suggested that he apply it to produce lead chromates. Fresh galena was put into a solution 'plus ou moins étendue' of potassium dichromate. After six months the galena was covered with a mixture of yellow, green and red compounds and the red (insoluble in water) was shown by physical properties to be phoenicochroite.<sup>1</sup> L. Bourgeois (1887) described a method for synthesizing crocoite and presented an analysis of the product. He also noted that the red rectangular tablets produced by Liebig and Wöhler could well be melanochroite and, moreover, isomorphous with lanarkite. Recent work has confirmed this guess regarding the isomorphism of lanarkite and phoenicochroite.

M. Lachaud & C. Lepierre (1890, 1891) dissolved lead chromate in hot 2N KOH solution and obtained yellow-orange prismatic crystals which gave, upon analysis: PbO 82.01%, 81.85; CrO<sub>3</sub> 17.95, 18.02, totalling 99.90, 99.87. They also obtained a product of rich red colour by fusing lead chromate with salt and obtained two analyses: PbO 77.20%, 77.25; CrO<sub>3</sub> 22.55, 22.90, totalling 99.75 and 100.15. This product was stated to be orthorhombic with a specific gravity of 5.81, and was regarded as synthetic melanochroite. Another fusion product was analysed and gave a composition near Pb<sub>4</sub>Cr<sub>5</sub>O<sub>16</sub>. Shortly after, C. Ludeking (1892) claimed that he synthesized crocoite and phoenicochroite by permitting a solution of PbCrO<sub>4</sub> in concentrated KOH to evaporate slowly in air for several months. His analyses are: 'crocoite', PbO 63.9%, CrO<sub>3</sub> 35.2, 99.1 total, and 'phoenicochroite' PbO 71.2%, CrO<sub>3</sub> 25.9, total 97.1. An excess of KOH was said to favour the formation of phoenicochroite; an excess of PbCrO<sub>4</sub>, crocoite.<sup>2</sup>

M. Gröger (1919) prepared a clear red basic lead chromate using the fusion methods employed by Liebig and Wöhler. Analysis of the product gave: PbO 81.08%, CrO<sub>3</sub> 18.85 and CrO<sub>3</sub> 19.06, 19.00, 19.00, the chromate being determined iodometrically. His main concern was proving the efficacy of the iodometric method; his product has been assumed to be phoenicochroite. J. F. G. Hicks (1921) prepared a number of basic lead chromates by fusion of PbO and either sodium or potassium chromate in a flux of KNO<sub>3</sub> or NaNO<sub>3</sub>. He claimed that the following salts were obtained: PbO : PbCrO<sub>4</sub> = 1 : 2, 1 : 1, 2 : 1 and 3 : 1. Analyses were made of fine-grained reaction products. A widely quoted paper by F. Jaeger & H. Germs (1921) dealt with the system PbO-PbCrO<sub>4</sub> up to 900 °C. They found: PbO : PbCrO<sub>4</sub> = 4 : 1, 5 : 2, 1 : 1 and crocoite. They failed to find salts with ratios of 2 : 1 or 1 : 2, and expressed doubt about the existence of the 5 : 2 salt (presumed to be phoenicochroite). R. Weinland & F. Paul (1923) claimed that they grew fire-red crystals from solution which yielded, upon analysis, Pb 75.76%, CrO<sub>4</sub> 20.86. They also grew, from perchloric acid solutions, a compound said to be PbO.2PbCrO<sub>4</sub> analysing 70.97% Pb.

H. Wagner *et al.* (1932) also discussed the basic lead chromates and gave X-ray data for some of their artificial products. They reported a tetragonal chromate but are vague about its composition; it could be (they said) PbCrO<sub>4</sub>.PbO.*n*H<sub>2</sub>O

<sup>1</sup> My own attempts with a variety of solutions 'plus ou moins étendue' have invariably failed to produce phoenicochroite.

<sup>2</sup> I have tried this method with a considerable range of solution compositions. Bright red crystals could be obtained but were invariably litharge.

mixed more or less with  $\text{Pb}_2\text{CrO}_4(\text{OH})_2$ . H. Wagner & H. Schirmer (1935) corrected Wagner's earlier statements about the vaguely defined compound of Pb,  $\text{CrO}_4$  and more or less OH and  $\text{H}_2\text{O}$ . This could now be shown to be  $\text{Pb}_2\text{CrO}_5$ , which appeared tetragonal under the microscope, and gave an X-ray powder pattern compatible with a tetragonal cell having  $a$  5.95,  $c$  6.71 Å.

L. Cloutier (1933) reviewed the conflicting reports on the basic lead chromates and investigated the aqueous system  $\text{Pb}(\text{NO}_3)_2/\text{K}_2\text{CrO}_4/\text{KOH}$ . He analysed solution compositions after precipitation and concluded that he could only obtain  $\text{PbO} \cdot \text{PbCrO}_4$  and  $2\text{PbO} \cdot \text{PbCrO}_4$ . He was sceptical of other salts reported by Hicks and by Jaeger & Germs.

#### FORNACITE

A new chromate mineral was described by A. Lacroix in 1915. It occurred as small crystals in a 'magnificent' geode of diopside from Djoué, French Equatorial Africa (now part of Zaïre). No analyses were given but qualitative tests showed that it was an arsenate-chromate of lead and copper. He considered its possible identity with vauquelinite but said the new mineral differed because it carried hydroxide as well as oxide radicals, i.e. it was a basic salt. The colour was given as olive green ('like Cornish olivenite') with a yellow streak. The name given was 'furnacite' but this was soon corrected to fornacite (from *fornax*, in honour of L. Fourneau; Lacroix, 1916).

An analysis of fornacite, however, had to wait for C. Guillemin & J. Prouvost (1951), who showed that it is the arsenic analogue of vauquelinite. They also gave two new analyses of Berezov vauquelinite for comparison, though one of their specimens had the locality given simply as Ekaterinburg. X-ray powder data, new specific gravity determinations, optics and spectrographic analyses were also included. They proposed to call such minerals containing more than 7% by weight  $\text{As}_2\text{O}_5$  fornacite, others vauquelinite (the 50 mols% division would be at 7.62%  $\text{As}_2\text{O}_5$ ).

P. Bariand & P. Herpin (1962) examined fornacite from a new locality (Sebarz, Iran) and provided a new analysis and an indexed X-ray powder pattern. They concluded that it is a valid and distinct species.

#### EMBREYITE

F. Pisani (1880) published another new mineral description based on Berezov material. This was referred to as chromo-phosphate of lead and copper and was not given a name. His description deserves more careful attention than it has received. He wrote that it was botryoidal, *red-orange* with a yellow streak, and had a drusy crystalline surface. To these few tantalizing comments only a chemical analysis was added: PbO 70.60%, CuO 4.57,  $\text{CrO}_3$  15.80,  $\text{P}_2\text{O}_5$  9.78.

In 1968 I found orange to yellow-brown crystalline material on Berezov specimens in the collections of the École des Mines, Paris and on British Museum (Natural History) specimen BM 94718 that matched data obtained on a specimen belonging to Mr John B. Jago of San Francisco that I had seen in 1963. With this supply of

better material I undertook the description of a new species, to be named embreyite (Williams, 1972). It is a chromate-phosphate of lead and copper very similar to and probably identical with that described, incompletely, by Pisani (1880), and was possibly first noted by Macquart (1789). Further specimens of this mineral were subsequently found at the British Museum (Natural History) in 1971.

On some of these specimens (BM 94718 and 39319) there is also massive oily green to brown material which shows, spectrographically, Pb, Cu, Cr and P. X-ray powder patterns of this material are rich in lines and suggest that it is a mixture. However, the strong lines in these patterns (several have been taken) do not match any of the other lead chromates. A description will have to await the availability of better material.

#### IRANITE AND HEMIHDRITE

P. Bariand (1963) found a number of chromates at Sebarz, Anarak, Iran, and together with P. Herpin described a new mineral, iranite, from this locality (Bariand & Herpin, 1963). After microprobe analysis for Pb and Cr, and proof of the presence of water by the Penfield method, they assigned the formula  $\text{PbCrO}_4 \cdot \text{H}_2\text{O}$ . The water had been determined by difference. The mineral was described as orange, occurring as small, measurable triclinic crystals associated with a variety of lead, copper and zinc minerals.

Hemihedrite was described by S. A. Williams & J. W. Anthony (1970) as a new triclinic lead zinc chromate from the Florence Lead Silver mine in Arizona. Its composition appeared to be unlike that of iranite, and its powder pattern lacked many of the lines given by Bariand & Herpin for iranite. Recent work has shown, however, that the formula of iranite was incorrectly given, and that numerous misprints appeared in the intensities presented in the powder pattern (Bariand, pers. comm., 1973). New partial analyses have shown the following: Sebarz, type iranite 4.59% CuO, 0.20 ZnO; Seh-Changi, Iran, iranite 2.29% CuO, 0.43 ZnO; Potter-Cramer, Arizona, hemihedrite 0.04% CuO, 2.49 ZnO; Boulder City, Nevada, hemihedrite 0.58% CuO, 1.30 ZnO. Although further work needs doing, it is possible that a series from iranite (Cu end member) to hemihedrite (Zn end member) may be the solution to the problem. Work done to date shows that both species are valid and closely related.

A recent paper by Adib *et al.* (1972) tends to confirm this; an X-ray study of topotype material shows that their 'khuniite' is iranite. The role played by fluorine and hydroxyl in these minerals is still uncertain, but I believe the problems can be solved without the introduction of an abundance of mineral names.

#### SANTANAITE

The most recently described lead chromate santanaite (Mücke, 1972), occurs sparingly at the Santa Ana mine in Chile. As described, this mineral appears to be totally unlike any previously known lead chromate. A formula  $\text{Pb}_{11}\text{CrO}_{16}$  has been





FIG. 7. Hemihedrite, Arizona ; after Williams and Anthony, 1970.

assigned, but the oxygen was determined by difference with a probable error of  $\pm 2\%$ , so that the composition could lie anywhere in the range  $\text{Pb}_{11}\text{CrO}_{13}$  to  $\text{Pb}_{11}\text{CrO}_{19}$ .

#### SOME DOUBTFUL SPECIES

*Jossaite*. Breithaupt (1858) described another species from Berezov. No chemical analysis was given but chemical tests by Plattner, cited in his paper, indicated that it was a chromate of lead and zinc and, possibly, cadmium. The specific gravity was 5.2 but Breithaupt was clearly not confident of this value. A prism angle of  $110^\circ$  to  $118^\circ$  was also given. The colour was orange. Breithaupt had kept the material for six years hoping to get more for a complete description and then, giving up, published this short note. Jossaite has never had much success as a mineral. Only B. Silliman, Jr (1881) has reported it from elsewhere, namely on a suite of specimens sent to him from a locality 20 miles north-east of Vulture P.O. in Arizona. A number of collectors, notably the late Ed McDole (deceased, 1970), have searched for this locality in vain. Recently I found a fine suite of chromates the same distance from Vulture P.O. but in exactly the opposite direction. Among these was a chromate of lead and zinc, but it does not fit Breithaupt's scanty description. Furthermore, I have examined a specimen of 'jossaite' from the U.S. National Museum (R 6032) and shown it to be crocoite; it fitted Breithaupt's description rather well.<sup>1</sup> Jossaite remains a mystery and is probably a myth.

A. Arzruni (1885), in an important contribution to the geology of the Berezov area, lists the minerals found in the district:<sup>2</sup> anglesite, azurite, beudantite, bindheimite, bismutite, bismuth ochre, calcite, caledonite, cerussite, chalcedony, chalcopryrite, chlorite, chromite, chrome ochre, chrysocolla, covellite, crocoite, dolomite, fuchsite, galena, garnet, goethite, gold, hematite, hydrohematite (= turgite), jarosite, jossaite, laxmannite, leadhillite, limonite, linarite, magnetite, malachite,

<sup>1</sup> One might wonder if the mineral could be hemihedrite. I have seen none on Berezov specimens nor, for that matter, have I seen *any* zinc minerals. The only zinc mineral reported by Arzruni (1885) is Jossaite (!) of which he asks '... ist der Zinkgehalt unzweifelhaft?'

<sup>2</sup> Most authors agree that the Berezov district lies within a rectangle seven versts east-west by eight versts north-south with Berezov at centre of the lower edge.

melanochroite, muscovite, orthoclase, patrinite, plagioclase, pyrite, pyromorphite, pyrophyllite, quartz, rutile, scorodite, sulphur, talc, tennantite, tetrahedrite, torbernite, tourmaline, tremolite, vanadinite, vauquelinite, wad, wulfenite, xanthosiderite and zircon.

Arzruni gave the Preobrazenskij mine as the locality for jossaitite but how he knew I have been unable to determine. In addition to this list, Arzruni gave abbreviated mineral lists for crocoite localities outside the Berezov district. At Bertjówajá Gorá it occurred with cerussite, galena, malachite, pyromorphite, pyrite and quartz, and at Tochil'naya Gora with pyrite, quartz and tourmaline containing, in one instance, 1.166%  $\text{Cr}_2\text{O}_3$ . This analysis is not his but that of H. R. Hermann.

*Eosite.* A. Schrauf (1871) described a new mineral from Leadhills in Scotland as eosite. His morphological data are exhaustively complete, and the crystals are clearly close to wulfenite, both in angles and habit. The chemical results are very fragmentary, however. He did only qualitative work, indicating that it was a vanadian wulfenite, and apparently did not look for chromium. Since we now know that a variety of chromates occur at Leadhills, it is possible that eosite contained chromate. I have not been able to find a specimen of the original eosite, however. A sample so labelled at the British Museum (Natural History) was stored among the doubtful species, but proved to be beautifully crystallized phoenicochroite showing several new forms and 'butterfly' twinning on  $\{20\bar{1}\}$ .

' $4\text{PbO} \cdot 3\text{CrO}_3$ '. W. E. Dawson (1886) sent a small sample to the British Museum (Natural History) from the Transvaal with an analysis showing PbO 74.76%,  $\text{CrO}_3$  25.24, and his letter to the Mineralogical Society was published in the *Mineralogical Magazine*. Correspondence files at the British Museum (Natural History) indicate that L. J. Spencer and G. T. Prior had quickly shown that the specimen (BM 62927) was merely red vanadinite; this was verified recently on the same material by C. J. Elliot by infra-red spectroscopy. Dawson's analysis, unfortunately, has been taken seriously by later workers. There is now no reason to believe the analysis, and the 'new chromate from the Transvaal' should be eliminated from further consideration.

*Beresovite* was described by Ya. Samoilov (Самойлов, Я.; Samoilow, J.) (1897). The type locality was Berezov but the material providing the new species came from a collection at the University of Moscow. Samoilov gave a fairly clear description of this mineral. It occurred in lamellar masses or intergrown crystals, which could not be measured but showed good cleavage. The specific gravity (6.69) was determined on 2.2 grams with a pycnometer. Associated species were cerussite, galena, and crocoite, which may replace it. Three partial analyses were given: 0.6972 g gave PbO 79.36%,  $\text{CrO}_3$  17.93; 0.6368 g gave PbO 79.24,  $\text{CrO}_3$  17.93; and 0.6387 g gave  $\text{CO}_2$  2.46. The mineral was said to be pleochroic, red to red-yellow when lying on its cleavage, and in this position it showed no trace of an interference figure.

G. Bischof (1866) called attention to the fact that phoenicochroite may alter to crocoite, and his paper shows the first real interest in the paragenesis of the Russian chromates. He believed that vauquelinite obtained its copper from malachite and linarite, which are earlier-formed species on some specimens. Bischof examined specimens from Berezov and Tochil'naya Gora but gave still another locality for



chromates: Bertewaja Gora, near Nischne-Tagilsk (Нижний Тагил, Nizhnii-Tagil, 57°54' N, 58°57' E). Further data on paragenesis were given by Cornu (1909).

Recent work, especially by R. J. Davis (unpublished), has called attention again to the tendency of phoenicochroite to alter to a mixture of crocoite and cerussite. Since in other respects Samoilov's description fits phoenicochroite well, it appears probable that beresovite is partially altered phoenicochroite.

Petterd also claimed (1902, 1903) that he had found beresovite, but he gave only a visual impression of the material. It was found at the Magnet mine as 'characteristic crystals', yellow to orange to crimson, implanted on a soft matrix.

*Bellite*. Petterd (1910) described a new mineral which he named bellite. It occurred at the Magnet Silver and Magnet mines, Tasmania, as delicate red or crimson tufts. Crystals were needles of hexagonal outline associated with chromian cerussite, crocoite and mimetite. The mimetite might be chromiferous, he said. The specific gravity was 5.5 and an analysis by J. D. Millen in London gave: PbO 61.680%, CrO<sub>3</sub> 22.611, V<sub>2</sub>O<sub>5</sub> 0.106, P<sub>2</sub>O<sub>5</sub> 0.045, As<sub>2</sub>O<sub>3</sub> (sic) 6.548, Al<sub>2</sub>O<sub>3</sub> 0.012, Cl 0.516, SO<sub>3</sub> 0.054, Ag tr., SiO<sub>2</sub> 7.587 totalling 99.159. This mineral was reinvestigated by Strunz (1958). The original description had been scanty and L. J. Spencer (1907) had said it was probably a mixture of mimetite, quartz and crocoite on the basis of the analysis. Strunz's X-ray work showed a strong similarity of the powder patterns of bellite (*a* 10.13, *c* 7.39 Å) and mimetite. Strunz considered the SiO<sub>2</sub> in the analysis to be essential; he wrote a formula, based on those of the lead apatites, essentially reinstating the species. Shortly afterwards W. Johnson (1960) succeeded in preparing a chromium analogue of hydroxyapatite, containing Cr<sup>3+</sup> and Cr<sup>6+</sup>, and no phosphate.

A recent (Tasm. Dept. Mines, 1970) partial analysis of presumed type material showed: PbO 70.0%, Cr<sub>2</sub>O<sub>3</sub> 2.9,<sup>1</sup> As<sub>2</sub>O<sub>3</sub> 14.5, Cl 2.5. The authors conclude that bellite is mimetite mixed, in their analysis, with crocoite in the approximate ratio of 10:1, thereby invalidating the species.

#### A SUMMARY OF THE VALID AND DOUBTFUL SPECIES

Of the minerals that have been discussed *crocoite* (PbCrO<sub>4</sub>) is truly the head of the family. It was the first found, is the most common and has suffered the least abuse at the hands of mineralogists during the past two and a half centuries. Its status or validity has never been questioned and it is now well described. Only its nomenclature has been confusing, and crocoite only gradually emerged as the accepted name after its first use by Breithaupt in 1841.

*Phoenicochroite* (Pb<sub>2</sub>CrO<sub>5</sub>) was noted as early, and its history is about as long as that of crocoite, but its description had to wait until 1833. It has suffered some name changes and was largely ignored except by chemists who continually reported its synthesis. The original analysis was faulty, and this has led to considerable confusion and some wishful thinking. Nobody has satisfactorily demonstrated that he can produce a red chromate matching H. R. Hermann's formula (2PbCrO<sub>4</sub>.PbO),

<sup>1</sup> The value 2.9% Cr<sub>2</sub>O<sub>3</sub> is compared with Petterd's (1910) value of 22.611% for CrO<sub>3</sub>, given here as 22.61% Cr<sub>2</sub>O<sub>3</sub>.

but over the years artificial preparations with compositions near  $\text{Pb}_2\text{CrO}_5$  have been obtained, and, as has been recently shown, this is the composition of phoenicochroite. Phoenicochroite alters readily to a mixture of crocoite and cerussite, and it was almost certainly such a mixture that Samoilov analysed and named *beresovite*. The recently described *scheibeite* and *chrominium* (p. 394–5) have the same unit cell constants and other properties as phoenicochroite and are clearly identical with it.

*Vauquelinite* ( $\text{Pb}_2\text{CuCrO}_4\text{PO}_4\text{OH}$ ) is the third lead chromate mineral to be recognized – it was described clearly by Macquart in 1789 but was not named for another 29 years. The original analysis was probably faulty, as Hermann (1870) maintained, but this has not cast any doubt on the validity of the species as was the case with phoenicochroite. But vauquelinite has undoubtedly been confounded not only with pyromorphite, but with embreyite and the intimate mixture of two or more other species that I have found. Scrutiny of analyses made by later workers strongly suggests that they have analysed mixtures. Further work, particularly analyses of pure Berezov material, is desirable.

*Fornacite* ( $\text{Pb}_2(\text{Cu},\text{Fe})\text{CrO}_4(\text{P},\text{As})\text{O}_4\text{OH}$ ) is probably isomorphous with vauquelinite according to the structural studies of Fanfani and his colleagues, but despite the dubious material that has been analysed in the past, there may well be a threefold series between the chromate, phosphate and arsenates of lead and copper. Analyses done to date, if believed, suggest considerable substitution of  $\text{CrO}_3$  for  $\text{P}_2\text{O}_5$ , and of  $\text{CrO}_3$  for  $\text{As}_2\text{O}_5$  and vice versa. Should further work support these views, laxmannite might well be reinstated for the phosphate end member.

*Iranite* and *hemihedrite* are remarkably similar, and at one time I thought they were identical. Recent electron probe analyses on Bariand's type specimen and his second occurrence material (also in Iran) have both shown less than 0.05% Zn, whereas hemihedrite has considerably more and contains no Cu. Since the unit cells of the two minerals can be transformed to near identity, and all other properties are very similar, it seems probable that there is a series, partial or complete, between the two species with Zn and Cu replacing one another.

*Embreyite*,  $\text{Pb}_5(\text{CrO}_4)_2(\text{PO}_4)_2\cdot\text{H}_2\text{O}$ , stands alone – it is unlike any other chromate mineral – but Pisani's analysis should probably be placed here (see p. 397). This analysis has previously been included with the vauquelinites, from which it differs mainly in having more lead and less copper. The other massive phases, known at present only by their powder patterns, are probably inextricably mixed in the chemical analyses of some of the Russian vauquelinites. More work needs to be done.

*Santanaites* is clearly a valid species, though its formula remains uncertain.

*Eosite* remains a mystery. Artificial tetragonal lead chromates have been described, but whether they are completely isomorphous with the lead molybdates is doubtful. It is not even certain yet whether or not eosite should be classed as a molybdate-vanadate or a molybdate-chromate. More work needs to be done, and Schrauf's original material, if it could be found, would be essential for this.

*Bellite* may eventually stand as a valid species even if the original analysis was carried out on a mixture. Chromate can enter into mimetites or similar structures,



and a chromate analogue of apatite has been artificially prepared. There is an abundance of such minerals at Leadhills and in the Arizona (Wickenburg) locality, and some of these Arizona mimetites are highly chromatian. Analysis of a specimen from Wanlockhead (Vernon, 1827) showed only 1.20%  $\text{PbCrO}_4$ , however; and Temple (1956) found less than 1% Cr in a Leadhills specimen (pers. comm., 1964). Discrediting the Tasmanian material need not affect the potential validity of the mineral.

*Jossaite* is difficult to discredit since there are no authentic specimens, to my knowledge, extant. A specimen from the United States National Museum (catalog R6032) did not have good credentials, but it is highly suggestive that the crystals on this piece fit Breithaupt's description well – and are crocoite. I have seen no sign of the lead zinc chromate hemihedrite in the Berezov material, and in fact have not yet seen any zinc mineral from that locality: so jossaite must remain highly doubtful. One must wonder, however, about the positive zinc test jossaite gave Plattner; also bothersome is the fact that Breithaupt considered jossaite younger than vauquelinite. On Berezov specimens it is usually obvious that crocoite is older.

#### SUMMARIZED DATA FOR THE SEVERAL SPECIES

##### Crocoite, $\text{PbCrO}_4$ ; monoclinic, $2/m$

Some other names are: *minera plumbi specie crystalline rubra* (Lehmann, 1766, 1767); *plomb rouge* (Davila & de l'Isle, 1767; also Sage, 1769); *mine de plomb rouge* (Pallas, 1770); *plumbum hexaedrum rhombeum fulvum* (de l'Isle, 1772); *roth bleyerz* (Werner, 1774); *minera plumbi rubra* (Wallerius, 1778); *red lead spar* (Kirwan, 1784); *oxide de plomb combiné avec oxide de fer* (Born, 1790); *plomb minéralise par l'air pur* (Bergmann *et al.*, 1792); *plomb chromaté* (Haüy, 1801); *Kallochrom* (Hausmann, 1813); *chromate of lead* (Phillips, 1823); *hemiprismatischer Blei-baryt* (Mohs, 1824); *chromsaüres Blei* (von Leonard, 1826); *crocoïse* (Beudant, 1832); *Chromspath* (Breithaupt, 1832); *Crocoisite* (von Kobell, 1838); *Krokoit* (Breithaupt, 1841); *lehmannite* (Brooke & Miller, 1852); *beresofite* (Shepard, 1852).

*Physical properties*: Crocoite is bright to dull orange to orange-red with an orange streak. Typical Berezov specimens gave colour matches (Royal Horticultural Society) such as 34C (grenadine red), 44B and 32A (indian orange). A typical Dundas specimen was 41B (vermilion). The streak is 23A (cadmium orange) to 24A (tangerine orange).

Specific gravities ranging from 5.75 to 6.29 have been reported;<sup>1</sup> the more reliable data range from 5.99 to 6.12 (calc. for  $\text{PbCrO}_4$  with Pistorius & Pistorius cell dimensions, 6.11). H.  $2\frac{1}{2}$  to 3.

Crocoite is slightly pleochroic in shades of orange;  $\alpha$  2.29,  $\beta$  2.36,  $\gamma$  2.66 all  $\pm 0.02$ ,  $2V_\gamma$   $57^\circ$ , all for Li (Larsen, 1921);  $2V_\gamma$   $54^\circ 3'$  for Na,  $\beta \parallel [010]$ ,  $\gamma: [001]$   $5^\circ 30'$  in the obtuse angle  $\beta$  (Des Cloizeaux, 1882).

<sup>1</sup> 6.0269, Brisson, 1787; 5.75, Bindheim, 1792; 6.004, Haidinger, 1825; 6.004, Breithaupt, 1841; 6.118, Manross, 1852; 5.965, Schröder, 1874; 6.29, Bourgeois, 1887; 5.92, Liversidge, 1895; 7.123, Schulten, 1904; 6.06, Quareni & Pieri, 1964; 6.12, Laurent *et al.*, 1967.

*X-ray data*: The space-group is  $P2_1/n$  (Quareni & Pieri, 1964);  $Z = 4$ . Cell dimensions have been determined by several authors (Gossner & Mussnug interchanged the  $a$  and  $c$  axes):

	$a$	$b$	$c$	$\beta$	Locality
Gossner & Mussnug, 1930*	7.17 Å	7.49	6.83	102°27'	} Not stated
Brill, 1931*	7.11	7.40	6.81	n.d.	
Gliszczynski, 1939*	7.122	7.425	6.785	103°38'	Berezov
Pistorius & Pistorius, 1962†	7.122	7.425	6.785	102°27'	Berezov
Williams, on B.M. 40448	7.120	7.421	6.800	102°20'	Berezov

\* Cell dimensions converted from kX.

†  $a, b \pm 0.006$ ;  $c \pm 0.004$ .

The strongest X-ray powder diffractions reported are:

	Pistorius & Pistorius, 1962 Synthetic		Williams BM 40448 Berezov		Williams USNM R6032 Berezov <sup>1</sup>		Williams Wickenburg	
$hkl$	$d$	$I$	$d$	$I$	$d$	$I$	$d$	$I$
011	4.951 Å	18	4.950 Å	3	4.935 Å	3	4.939 Å	5
11 $\bar{1}$	4.378	27	4.374	5	4.372	4	4.370	6
200	3.476	85	3.475	8	3.479	9	3.477	10
10 $\bar{2}$ , 120	3.276	100	3.277	10	3.273	10	3.274	10
210	3.148	18	3.150	1	3.149	2	3.150	2
012	3.027	30	3.030	6	3.017	8	3.018	9
10 $\bar{3}$ , 13 $\bar{1}$ , 221	2.253	19	2.254	5	2.250	4	2.250	6
132, 32 $\bar{2}$	1.846	21	1.846	3	1.848	4	1.848	6

<sup>1</sup> 'Jossaite'.

*Chemistry*: In the following table of analyses, the original data have been recalculated using modern atomic weights wherever the author has described his methods in sufficient detail. In several cases computational errors in the original have been found.

	1	2	3	4	5	6	7	8
PbO	53.9%	46.3	65 to 77	64.6	38.9	60.8	65.0	62.2
CrO <sub>3</sub>	—	—	—	—	—	[39.2]*	24.9	[37.8]*
	9	10	11	12	13	14	15	
PbO	+	67.91	68.50	68.82	66.86	68.35	69.06	
CrO <sub>3</sub>	+	31.725	31.76	31.16	30.99	30.35	30.94	

\* By difference.

- Lehmann, 1769
- Pallas, 1773; also Ag present
- Sage, 1777; also Fe and Cl present
- Bindheim, 1792; also Fe<sub>2</sub>O<sub>3</sub> 1%, MoO<sub>3</sub> 11.7, SiO<sub>2</sub> 4.5, NiO 5.7, CaO 6, volatiles 5, Ag trace.
- Macquart, 1789; also Al<sub>2</sub>O<sub>3</sub> 5.1%
- Vauquelin, 1797
- Richter, 1800; also impurities 10.1%
- Thénard, 1800
- Sage, 1800; Sb 45%, Al<sub>2</sub>O<sub>3</sub> present
- Pfaff, 1816
- Berzelius, 1818
- Baerwald, 1882
- Liversidge, 1895
- Laurent, 1967; also SiO<sub>2</sub> 1.10%
- Theory for PbCrO<sub>4</sub>



*Paragenesis*: Crocoite has a fairly broad range of stability in the paragenesis of chromates. It may form very early but is later than anglesite and phoenicochroite. At Berezov it is often earlier than cerussite, and has formed at the expense of phoenicochroite or by replacement of anglesite. This is particularly true of those partially oxidized specimens with remnants of fresh galena. With continuing oxidation crocoite may form along with cerussite, and in such cases it may be deposited on fracture surfaces some distance from the 'parent' galena. If copper or zinc is present crocoite is eventually replaced by iranite, hemihedrite or vauquelinite.

Phoenicochroite,  $\text{Pb}_2\text{CrO}_5$ ; monoclinic,  $2/m$

The nomenclature of phoenicochroite was: Melanochroit (Hermann, 1833); Phönikochroit (Glocker, 1839); Phönicit (Breithaupt, 1841); Phönicit (Haidinger, 1845); phoenicochroite (Nicol, 1849); phoenicite (Brooke & Miller, 1852); Phönizit (Breithaupt, 1852); *beresowite* (Samoilow, 1899); *scheibeite* (Mücke, 1970); *chrominium* (Adib & Ottemann, 1970). It was probably the mineral 'the colour of Japanese cinnabar' noted by Lehmann (1766).

*Physical properties*: Phoenicochroite is rich cochineal red with an orange or yellow-orange streak. H.  $2\frac{1}{2}$ . Specific gravity 7.01 (calc. for  $\text{Pb}_2\text{CrO}_5$ , 7.07). Crystals tend to be tabular prisms and exhibit a very smooth cleavage on  $(\bar{2}01)$ . The refractive indices are: for Li,  $\alpha$  2.34,  $\beta$  2.38,  $\gamma$  2.65 (Larsen, 1921); for Na,  $\alpha$  2.38,  $\beta$  2.44,  $\gamma$  2.65, with  $2V_\gamma$   $58^\circ$ ,  $\alpha \parallel [010]$ ,  $\beta : [001]$   $2^\circ$  in the obtuse angle  $\beta$  (Williams, 1970).

*X-ray data*: The space-group is  $C2/m$ ;  $Z = 4$ ; the following cell dimensions have been transformed to the setting of Williams *et al.* (1970) for comparison

	<i>a</i>	<i>b</i>	<i>c</i>	$\beta$	Locality
Bariand, unpubl.	14.17 Å	5.68	7.13	$114^\circ 10'$	Iran
Adib & Ottemann, 1970	14.16	2.84	7.10	$115^\circ 30'$	Anarak, Iran
Mücke, 1970	14.032	5.679	7.138	$115^\circ 16'$	Sierra Gorda, Chile
Zemann, 1970	14.00	5.68	7.14	$115^\circ 30'$	Anarak, Iran
Williams <i>et al.</i> , 1970	14.001	5.675	7.137	$115^\circ 13'$	Berezov
Williams, on BM 39316	13.993	5.667	7.130	$115^\circ 16'$	Berezov

The strongest X-ray powder diffractions reported are:

	Temple, 1956 Leadhills		Williams BM 39316, Berezov		Williams Harvard 67151, Berezov		Williams <i>et al.</i> , 1970 Wickenburg	
<i>hkl</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
001	6.49 Å	m	6.437 Å	3	6.389 Å	8 B	6.43 Å	5
200	—	—	6.318	3				5
310	3.38	vs	3.383	10	3.387	10	3.380	10
$\bar{1}12$ , $40\bar{2}$ , $41\bar{1}$	2.98	vs	2.979	10	2.981	10	2.979	10
020	2.86	s	2.834	4	2.836	6	2.831	5
202	2.48	fs	2.476	2	2.477	5	2.475	4
602	2.26	fs	2.264	4	2.261	7	2.263	4
$71\bar{2}$ , 222, $421$	1.87	s	1.868	5	1.867	8 B	1.862	5

*Chemistry :*

	1	2	3	4	5	6	7
PbO	76.69%	79.30	81.9	81.9	85.67	80.88	81.70
CrO <sub>3</sub>	[23.31]*	17.93	16	18.3	14.50	18.08	18.30

1. Berezov ; Hermann, 1833

2. Berezov, 'beresovite' ; Samoilow, 1897 ; also CO<sub>2</sub> 2.46%

3. Iran ; Bariand

4. Anarak, Iran, 'chrominium' ; Adib &amp; Ottemann, 1970

5. Sierra Gorda, Chile, 'scheibeite' ; Mücke, 1970

6. Wickenburg ; Williams *et al.*, 19707. Theory for Pb<sub>2</sub>CrO<sub>5</sub>

\* By difference.

*Paragenesis.* Phoenicochroite is readily distinguished by its deep red colour and cleavage. It is the first chromate to form and at Berezov it may occur directly upon anglesite, which films galena ; in fact there usually is some fresh galena in specimens containing phoenicochroite. Crocoite follows phoenicochroite in the paragenesis and, with cerussite, may form fine-grained pseudomorphs after phoenicochroite. At the Rat Tail claim (Arizona) phoenicochroite occurs as corroded blebs in clear, sharply euhedral cerussite crystals, and at the Potter-Cramer (Arizona) prospect it occurs in veinlets cutting the host rocks and is partially altered to cerussite stained bright orange by crocoite.

Vauquelinite, Pb<sub>2</sub>CuCrO<sub>4</sub>PO<sub>4</sub>OH, and fornacite, Pb<sub>2</sub>(Cu,Fe)CrO<sub>4</sub>(As,P)O<sub>4</sub>OH, monoclinic

Names for vauquelinite include : plomb vert noirâtre cunéiforme (Macquart, 1789) ; chromsäures Kupfer (Karsten, 1808 ; Ullmann, 1814) ; vauquelinite (Berzelius, 1818) ; Chromphosphorkupferbleispath (John, 1845) ; Laxmannit (Nordenskjöld, 1867) ; Phosphorchromit (Hermann, 1870).

Fornacite (Lacroix, 1915, 1916) has had no synonyms (furnacite was an error).

*Physical properties :* Both these minerals are pistachio green to almost black, with a dirty yellow streak. H. 2½ to 3. Specific gravities range from 5.986 to 6.12 for vauquelinite (calc. 6.16 on Williams' cell, 6.22 on Fanfani & Zanazzi's cell) ; 6.12 to 6.27 for fornacite (6.33 calc. on Cocco *et al.*'s cell, 6.47 on Bariand & Herpin's cell ; both these for the end-member Pb<sub>2</sub>CuCrO<sub>4</sub>AsO<sub>4</sub>OH).

Vauquelinite has  $2V_{\alpha} \approx 0^{\circ}$ ,  $\alpha$  2.11,  $\beta$  and  $\gamma$  2.22 (Larsen, 1921 ; Guillemin & Prouvost, 1951). Fornacite has  $2V$  near  $90^{\circ}$ ,  $\alpha$  2.14,  $\gamma$  2.24 (Guillemin & Prouvost, 1951 ; Bariand & Herpin, 1962).

*X-ray data :* The space-group for both species is  $P2_1/n$  ;  $Z = 4$ . Cell dimensions have been determined by several authors ; in the following table these have been converted to Berry's vauquelinite orientation (the morphological setting used by Dana (1951) may be transformed to Berry's setting by the matrix  $[30^-/0\bar{1}0/10\bar{1}]$ ) :



	<i>a</i>	<i>b</i>	<i>c</i>	$\beta$	Locality
Berry, 1949	13.68 Å	5.83	9.53	93°58'	Vauquelinite, Berezov
Fanfani & Zanazzi, 1968	13.754	5.806	9.563	94°34'	
Williams, on BM 40448	13.726	5.776	9.542	94°55½'	
Bariand & Herpin, 1962	13.60	5.91	9.63	95°59'	Sebarz
Cocco <i>et al.</i> , 1966	13.827	5.893	9.694	94°52'	Réneville
Williams	13.818	5.870	9.619	94°40'	Tiger
	13.831	5.899	9.698	94°47'	Congo

The strongest X-ray powder diffractions reported are :

Vauquelinite				Fornacite					
Guillemin & Prouvost, 1951 Berezov		Williams on BM 40448 Berezov		Bariand & Herpin, 1962 Sebarz		Williams			
						Tiger		Congo	
<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
4.54 Å	F	4.696 Å	7	4.80 Å	9	4.770 Å	5	4.812 Å	8
3.20	F	3.280	10	3.31	10	3.311	10	3.324	10
2.83	F	2.887	5	2.88	10	2.913	6	2.916	8
—	—	2.760	4	2.80	10	2.795	5	2.812	8
2.70	M	2.689	4	2.71	9	2.714	5	2.732	7
2.26	M	2.298	7	—	—	2.324	4	2.338	6
1.86	F	1.887	7	—	—	1.899	4 B	1.901	7
1.82	F	1.844	4	—	—	1.858	3	1.860	5

F = forte, B = broad

*Chemistry* : Chemical analyses of these minerals are reported below and have been recalculated where necessary, using modern atomic weights. I am very dubious of some of these results, particularly on Berezov vauquelinite, since it is very easy to obtain mixtures from what appears to be a uniform crust of dark green 'vauquelinite'.

	1	2	3	4	5	6	7
PbO	63.44%	60.87	50.1	61.26	61.06	68.33	62.70
CuO	11.20	10.80	11.20	12.43	10.85	7.36	9.58
CrO <sub>3</sub>	14.09	28.33	21.40	15.26	16.76	10.13	11.95
P <sub>2</sub> O <sub>5</sub>	10.00	—	4.10	8.05	8.57	9.94	9.23
Fe <sub>2</sub> O <sub>3</sub>	—	—	—	1.09	1.28	2.80	—
H <sub>2</sub> O <sup>+</sup>	1.27	—	1.78	1.31	0.90	1.16	—
Rem.	—	—	11.42	—	—	—	—
Lost	—	—	—	—	—	—	3.00

	8	9	10	11	12	13	14	15
PbO	62.59%	62.06	57.7	63.7	62.6	58.3	57.16	59.74
CuO	12.19	10.31	10.2	8.9	8.2	13.27	10.91	10.55
CrO <sub>3</sub>	21.46	17.44	15.3	14.4	15.2	7.37	11.78	13.27
P <sub>2</sub> O <sub>5</sub>	3.55	8.66	0.4	8.4	6.8	—	0.66	—
As <sub>2</sub> O <sub>5</sub>	—	—	13.4	0.2	2.6	20.00	15.03†	15.25
Fe <sub>2</sub> O <sub>3</sub>	0.70	0.50	0.2	1.7	1.4	—	0.40	—
H <sub>2</sub> O <sup>+</sup>	—	—	1.5	1.5	1.5	2.00*	2.05	1.19
H <sub>2</sub> O <sup>-</sup>	—	1.12	0.9	0.7	0.8	—	1.68	—

\* Considered non-essential by the authors who state that the mineral is anhydrous.

† Misprinted as As<sub>2</sub>O<sub>3</sub> in the original paper.

1. Vauquelinite; theory for  $\text{Pb}_2\text{CuCrO}_4\text{PO}_4\text{OH}$
2. Vauquelinite, Berzelius, 1818
3. Vauquelinite (Chromphosphorkupferbleispath), John, 1845
- 4 and 5. Vauquelinite (Laxmannite), Nordenskiöld, 1867
6. Vauquelinite (Phosphorchromite), Hermann, 1870
7. Vauquelinite, Nicolajew, 1878
- 8 and 9. Vauquelinite, Chirva, 1935
10. Fornacite, Guillemin & Prouvost, 1951
- 11 and 12. Vauquelinite, Guillemin & Prouvost, 1951
13. Fornacite, Smol'yaninova & Senderova, 1959
14. Fornacite, Bariand & Herpin, 1962
15. Fornacite; theory for  $\text{Pb}_2\text{CuCrO}_4\text{AsO}_4\text{OH}$

*Paragenesis*: Vauquelinite and fornacite tend to be late-formed oxide-zone minerals. They may be perched on and replace earlier crocoite, hemihedrite or embreyite, but are just as often transported, and occur in fractures in nearby wall-rocks. In some cases, it appears that chromate-bearing solutions derived from dissolution of crocoite have attacked cerussite, and vauquelinite may be perched on and in pits in cerussite crystals.

#### Embreyite, $\text{Pb}_5(\text{CrO}_4)_2(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ : monoclinic

Older nomenclature includes: mineral 'theils dunkel ochrebraun, theils dunkel leberbraun . . . zeisiggrünes Pulver' (Hausmann, 1813); 'nelken- und haar-braunes Erz . . .' (John, 1845); chromo-phosphate de plomb et de cuivre (Pisani, 1880); possibly also 'oxide jaune ou ocre de plomb' (Macquart, 1789).

*Physical properties*: Embreyite is orange or henna in colour with a specific gravity of 6.42 (calc. for Cu-free, 6.40). Refractive indices:  $\alpha$  2.20,  $\beta$ ,  $\gamma$  2.36;  $2V_\alpha \approx 0^\circ$ .  $\beta = [010]$ .

*X-ray data*: Crystals are ill-formed and known only by their X-ray cell:  $a$  9.755 Å,  $b$  5.636,  $c$  7.135,  $\beta$   $103^\circ 5'$ . Stronger lines of the powder pattern are: 4.751 (6), 3.563 (3), 3.475 (3), 3.167 (10), 2.818 (6), 2.608 (2), 2.314 (2), 2.213 (3), 2.187 (3), 2.105 (3), 1.917 (4).

*Chemistry*: Chemical analyses:

	1	2	3	4	5	6	7	8
PbO	72.25%	75.30	74.7	74.9	75.0	74.4	70.60	75.61
CuO	2.53	1.20	1.62	1.68	1.45	1.70	4.57	—
CrO <sub>3</sub>	13.08	—	13.4	13.5	13.6	13.4	15.50	13.55
P <sub>2</sub> O <sub>5</sub>	8.23	—	9.57	9.47	9.11	9.09	9.78	9.62
CO <sub>2</sub>	1.04	—	—	—	—	—	—	—
H <sub>2</sub> O	0.91	—	n.d.	n.d.	n.d.	0.91	—	1.22
ZnO	—	0.03	0.06	0.02	0.06	0.04	—	—
Fe <sub>2</sub> O <sub>3</sub>	—	0.01	0.01	0.04	0.01	0.02	—	—
Sum	98.04	—	99.4	99.6	99.2	99.56	100.45	100.00

1. Schwarzkopf Microanalytical Laboratory, analysts. Cu, Cr, Pb, by atomic absorption on 3.954 mg; H<sub>2</sub>O under N<sub>2</sub> at 800 °C on 7.724 mg; CO<sub>2</sub> on 7.725 mg, precipitated as BaCO<sub>3</sub>. P<sub>2</sub>O<sub>5</sub> on 1.582 mg; CO<sub>2</sub> from cerussite contamination. École des Mines specimen



2. J. A. Allen analyst, all elements by atomic absorption on 5.842 mg. École des Mines specimen
- 3, 4, 5. Analyses by electron probe by R. F. Symes and A. M. Clark, British Museum (Natural History), on BM 94718
6. Average of analyses after deducting cerussite from no. 1 and recalculating to 98.04%
7. Pisani, 1880
8.  $\text{Pb}_3(\text{CrO}_4)_2(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$

### Iranite and hemihedrite, anorthic

*Nomenclature* : Iranite (Bariand & Herpin, 1963) ; *khuniite* (Adib & Ottemann, 1970) is clearly identical with iranite. Hemihedrite (Williams & Anthony, 1970), is probably isomorphous with iranite.

*Physical properties* : Both minerals have a colour between brown and orange, with a yellow streak. The specific gravity of iranite has been determined as 5.9 and 6.1 ; that of hemihedrite is 6.42. The refractive indices are : iranite,  $\alpha$  2.25 to 2.30,  $\gamma$  2.40 to 2.50 (Bariand & Herpin, 1962) ; hemihedrite,  $\alpha$  2.105,  $\gamma$  2.65 (Williams & Anthony, 1970).

*X-ray data* : Iranite has  $a$  10.02 Å,  $b$  9.54,  $c$  9.89,  $\alpha$  104°30',  $\beta$  66°,  $\gamma$  108°30' (Bariand & Herpin, 1963). Hemihedrite has  $a$  9.497 Å,  $b$  11.443,  $c$  10.841,  $\alpha$  120°30',  $\beta$  92°6',  $\gamma$  55°50', or, in the same setting as iranite,  $a$  9.95,  $b$  9.50,  $c$  9.91,  $\alpha$  110°28',  $\beta$  66°10',  $\gamma$  107°58'.

The strongest X-ray powder diffractions are :

Iranite						Hemihedrite	
Bariand & Herpin, 1963		Williams on type material		Adib & Ottemann, 1970		Williams & Anthony, 1970	
$d$	$I$	$d$	$I$	$d$	$I$	$d$	$I$
4.84 Å	8	4.861 Å	7	4.877 Å	4	4.872 Å	9
4.42	8	4.372	6	4.370	6	4.364	8
3.28	10	3.282	10	3.294	10	3.301	10
3.18	10	3.174	10	3.185	9	3.164	8
3.08	10	3.086	9	3.081	7	3.102	8
2.935	5	2.917	4	2.922	5	2.924	5

*Chemistry* : The available chemical analyses of both minerals are imperfect : the fluorine determination in the hemihedrite analysis is probably high, and so is the water determination in the iranite analysis by Hey & Elliott, while Adib & Ottemann have not determined water, which is certainly present in iranite.

Empirical unit-cell contents have been calculated for hemihedrite, taking F by difference ( $F = 1.6\%$ ) ; the results agree well with the formula  $\text{ZnPb}_{10}(\text{CrO}_4)_6(\text{SiO}_4)_2\text{F}_2$  suggested by the structural work of McLean & Anthony (1970). For iranite, empirical unit-cell contents calculated from the mean of analyses 4 and 5, taking the specific gravity as 6.0, suggest the formula  $\text{CuPb}_{10}(\text{CrO}_4)_6(\text{OH})_{10}$ , analogous to that of hemihedrite with  $(\text{OH})_4$  replacing  $\text{SiO}_4$ .

	1	2	3	4	5	6	7		8	9
CuO	0.04	—	—	2.6	4.1	3.4	2.65	Cu	0.01	1.3
ZnO	2.85*	2.66	—	2.5	2.3	1.4†	—	Zn	1.1	0.5
PbO	72.74	73.05	66.2	74.0	72.3	73.1	74.36	Pb	9.9	9.6
CrO <sub>3</sub>	20.14	19.64	28.8	21.0	15.9	18.5	19.99	Cr	6.1	5.4
SiO <sub>2</sub>	3.31	3.93	—	—	—	—	—	Si	1.7	—
H <sub>2</sub> O	—	—	+	—	8.1	3.6‡	3.00	O	31.4	21.7
F	5.27	1.24	—	—	—	—	—	OH	—	11.8
	104.35	100.52	95.0	100.1	102.7	100.0	100.00	F	2.6	—
Less O≡F	2.21	0.52								

102.14 100.00

\* Mean of 3.93, 2.14 and 2.49.

† Mean of 2.5, 2.3, 0.20 and 0.43.

‡ By difference.

1. Hemihedrite, Williams & Anthony, 1970, with additional Zn determinations by Williams  
A specimen from Boulder City gave CuO 0.58%, ZnO 1.30
2. Hemihedrite, calculated for  $\text{ZnPb}_{10}(\text{CrO}_4)_6(\text{SiO}_4)_2\text{F}_2$ . Sp. gr. calc. 6.44 (obs. 6.42)
3. Iranite; Bariand & Herpin, 1963
4. Iranite ('khunite'); Adib & Ottemann, 1970
5. Iranite; Hey & Elliott (unpubl.) on 230  $\mu\text{g}$  of type material; colorimetric and atomic absorption analysis
6. Mean of 4 and 5, with additional Zn and Cu determinations by Williams
7. Iranite, calculated for  $\text{CuPb}_{10}(\text{CrO}_4)_6(\text{OH})_{10}$ . Sp. gr. calc. 6.14 (obs., 5.9, 6.1)
8. Hemihedrite. Empirical unit cell contents (see text)
9. Iranite. Empirical unit cell contents (see text)

*Paragenesis*: Iranite and hemihedrite form in the oxide zone at low Eh and probably in neutral to slightly alkaline waters. They may be expected to form after phenicochroite and anglesite and earlier than vauquelinite or embreyite. Crocoite and hemihedrite appear roughly contemporaneous at the Potter-Cramer mine.

#### Santanaite, hexagonal

Crystals are tabular yellow hexagonal and exhibit a good basal cleavage. Indices of refraction are  $\omega = 2.32$ ,  $\varepsilon = 2.12$ .

Stronger powder pattern lines are: 3.539 (10), 2.606 (8), 2.080 (5), 1.701 (5), 2.948 (4), 2.846 (4), 2.243 (4).

Electron probe analysis gave Pb  $88.0 \pm 2.0\%$ , Cr  $1.9 \pm 0.2$ , oxygen by difference, leading to  $\text{Pb}_{11}\text{CrO}_{(16 \pm 3)}$ .

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